

# PATENT SPECIFICATION

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## (54) MANUFACTURING TYPE A ZEOLITE DETERGENT BUILDERS

(71) We, MIZUSAWA KAGAKU KOGYO KABUSHIKI KAISHA, a Japanese Body Corporate of No. 2-22 Imbashi, Higashi-ku, Osaka, Japan, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for the preparation of type A zeolite detergent builders.

Alkali metal aluminosilicates such as zeolite have excellent water-softening ability, due to their high calcium ion exchange capacity, and have long been known as detergent builders.

The specification of our Japanese Patent No. 188,551 discloses a process for drastically treating acid clay or a similar clay with a mineral acid to dissolve out and remove substantially all components other than silica, and reacting the resulting activated silica with an alkali metal aluminate to form an alkali metal polysilicate and a water-insoluble solid alkali metal aluminosilicate corresponding in structure to a zeolite. This synthetic alkali metal aluminosilicate is valuable as a detergent builder, but the specification does not specifically disclose conditions under which an alkali metal aluminosilicate builder having an optimum combination of various washing-promoting properties will be obtained.

Important among washing-promoting properties of such builders are a metal ion sequestering property and a buffer capacity. Polyvalent metal ions contained in service water and stains, such as ions of calcium, magnesium and iron, react with surface active agents to form hardly water-soluble salts, resulting in drastic reduction of the surface activating capacity of detergents. Accordingly, it is important that detergent builders should have the ability to sequester ions of polyvalent metals such as calcium, i.e., an ion exchange ability.

In order to remove greasy stains, it is im-

portant that the pH of the washing liquid should be on the alkaline side, and it is therefore preferable that a substance having a buffer capacity under alkaline conditions should be used as a detergent builder.

Another property required of a detergent builder is that stains extracted in the washing liquid are absorbed and fixed so as not to cause re-contamination of washed fibrous articles with the removed stain material.

Since an alkali aluminosilicate builder is water-insoluble, it is important that the builder should have excellent dispersibility in a washing liquid and a good rinsing property. When the dispersibility of a water-insoluble solid builder is insufficient, the solid builder tends to adhere to washed articles and to reduce the rinsing property, and such troubles as so-called "powder falling", which is a phenomenon such that builder powder falls from a dried washed article, are often caused. Moreover, when a solid builder is composed of coarse particles, sedimentation or deposition of builder particles takes place in pipes for discharging washing liquids and such troubles as clogging of tubes and wearing of tube walls are caused.

Our Patent Application No. 47950/76 (Serial No. 1 571 003) describes and claims an improvement in the alkali metal aluminosilicate builder disclosed in the above-mentioned Japanese Patent No. 188,551, the improvement providing an optimum balance of properties. More specifically, that improvement provides a detergent builder comprising a finely divided powder of synthetic type A zeolite (as hereinafter defined) which has a degree of crystallisation (as hereinafter defined) in the range of from 35 to 75%, a primary particle size (as hereinafter defined) smaller than 1  $\mu$  and a secondary particle size (as hereinafter defined) smaller than 4  $\mu$ , a buffer capacity (S) (as hereinafter defined) of at least 132 ml/100 g of solids when titrated with 0.4N hydrochloric acid at a rate of 20 to 50 ml/hr, and a calcium ion binding ability (C.I.) (as hereinafter defined) of at least 70 mg/g expressed as CaO, and which

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in aqueous dispersion retains a uniformly negative surface potential after exchange of its sodium ions for calcium ions. This builder, in which substantially all of the particles have a primary particle size smaller than 1  $\mu$ , has in combination a high alkali buffer capacity, an excellent metal ion sequestering property, a high re-contamination preventing property, good dispersibility into a washing liquid, and good rinsing properties. Previously known builders were not readily obtainable as such fine powders, primary particle sizes of 1 to 3  $\mu$  or 3 to 5  $\mu$  being the smallest usually encountered.

The present invention relates to a process for preparing finely divided synthetic type A zeolite, in which substantially all of the particles have a primary particle size smaller than 1  $\mu$ .

This invention accordingly provides a process for the preparation of detergent builders, which comprises acid-treating a smectite clay mineral to prepare activated silica or activated alumina-silica under such acid-treating conditions (readily determinable as hereinafter described) that at least the X-ray diffraction peak of the plane index [001] is reduced to less than 15% of its original height, treating the resulting activated silica or activated alumina-silica with an alkali metal hydroxide or a water-soluble alkali metal silicate to prepare an alkali metal polysilicate or alkali metal polyaluminosilicate having a composition in which the  $\text{Na}_2\text{O}/\text{SiO}_2$  molar ratio is in the range of from 1/3.5 to 1/500, mixing said alkali metal polysilicate or alkali metal polyaluminosilicate with alumina and alkali metal components and water and aging the mixture if necessary to prepare a homogeneous mixture having a composition capable of forming zeolite of the type A, and heating said homogeneous mixture to crystallise out fine particles of synthetic type A zeolite (as hereinafter defined) having a primary particle size (as hereinafter defined) smaller than 1  $\mu$ .

The water-insoluble inorganic powder builders in question are described in detail in the aforementioned Application No. 47950/76 (Serial No. 1 571 003), but it is necessary to explain here that these builders have an X-ray diffraction pattern substantially the same as that indicated in Table B given hereinafter. That is, they have an X-ray diffraction pattern substantially the same as that of zeolite of the type A. The X-ray diffraction pattern is preferably determined by the following X-ray diffraction method using Cu-K $\alpha$  rays.

(1) Method for determination of X-ray diffraction pattern:

An X-ray diffraction apparatus manufactured by Rigaku Denki K.K. (X-ray generator Model Cat. No. 2171L and goniometer Model Cat. No. 4001) is used for this pre-

ferred determination. Conditions adopted are as follows:

Target: Cu  
Filter: Ni  
Voltage: 30 KV  
Current: 15 mA  
Count Full Scale: 500 C/S  
High Voltage: 1200 V  
Time Constant: 2 seconds  
Chart Speed: 2 cm/min  
Scanning Speed: 2°/min  
Divergency: 1°  
Receiving Slit Width: 0.3 mm

Each sample is first dried in a drier maintained at 110°C and pulverised in an agate mortar, and it is then used for the measurement.

TABLE B  
X-Ray Diffraction Pattern

Spacing d (KX)	Relative intensity (I/I <sub>0</sub> )
12.440	65.3
8.750	58.5
7.132	48.3
5.534	41.6
4.371	17.8
4.111	60
3.720	95.8
3.421	33
3.300	81.4
2.968	100
2.910	24.6
2.753	27.2
2.627	70.4
2.513	13.6
2.466	11.0

This pattern is typical of type A zeolites, and the references herein to an X-ray diffraction pattern "substantially the same" as the above X-ray diffraction pattern mean an X-ray diffraction pattern in which the relative intensity of each diffraction peak can be changed from the above-indicated value by  $\pm 30\%$ , preferably by  $\pm 20\%$ .

Zeolites include various kinds of differing chemical structure, for example, synthetic zeolites of types A, X, Y and T, chabazite, mor dentite, erionite, faujasite, clinoptilolite and sodalite hydrate. A synthetic alkali metal aluminosilicate having an X-ray diffraction pattern substantially the same (as hereinbefore defined) as the above X-ray diffraction pattern is hereinafter referred to as "a synthetic type A zeolite" and in order to enhance the washing-promoting activity of the builder, it is important that a synthetic type A zeolite be chosen.

The order of the X-ray diffraction peak intensity is sometimes changed depending on

the kind of the solid polysilicate used for the synthesis. For example, when a highly acid-treated clay material is used as the starting solid polysilicate, the intensity of the peak of the spacing  $d$  of 12.440 KX is higher than the intensity of the peak of the spacing  $d$  of 8.750 KX, but it is found that this order is reversed when a substantially less acid-treated clay mineral is used. Further, when a small amount of a sodalite hydrate crystal structure is present in the builder, the order of the intensity between the peak of the spacing  $d$  of 2.986 KX and the peak of the spacing  $d$  of 3.720 KX is reversed.

Since the builder is derived from a smectite clay mineral, it occasionally has, in addition to the above-mentioned X-ray diffraction peaks, those inherent in the starting clay mineral. It is often observed that the builder formed by using acid-treated acid clay shows small peaks typical of substances contained in this starting raw clay, for example, quartz ( $d=3.343$  KX), cristobalite ( $d=4.05$  KX) and feldspar ( $d=3.7697$  and  $3.1977$  KX). When the builder has a relatively low degree of crystallisation (described hereinafter), it is characterised in that its X-ray diffraction pattern has small peaks such as mentioned above.

(ii) Method for measurement of primary particle size ( $D_p$ ):

The term "primary particle size" is defined as a length of edge of the cubic zeolite particles directly measured by an electron microscope in a sample where respective particles are well dispersed. The measurement is preferably performed according to the following method.

A suitable amount of a sample is placed on a glass sheet, and paraffin wax or Vaseline (Registered Trade Mark) in a volume substantially equal to the volume of the sample is added to the sample. The mixture is sufficiently kneaded by a small stainless steel spatula, and a small amount of ethanol is further added and the mixture is further kneaded. The kneaded mixture is placed on a mesh for electron-microscopic measurement and immersed in ethanol to dissolve out the paraffin or the like. Then, the sample is dried for 1 hour in a drier maintained at 60 to 70°C to evaporate ethanol.

According to customary procedures, 4 electron-microscopic photographs suitable for the measurement of the primary particle size are taken from different vision fields at a magnification of 1,000 to 2,000 and the photographs are enlarged 10 times to obtain photographs having a total magnification of 10,000 to 20,000.

Among cubic particles taken on these photographs, 6 typical particles are chosen and among sides or edges of these particles, those deemed to be in parallel to the plane of the vision field (the mesh plane) are

chosen and the length of each of these sides is measured. The maximum value among the measured values is the primary particle size ( $D_p$ ).

Figure 1 illustrates an electron-microscopic photograph of commercially available zeolite of the type 4A, and Figure 2 illustrates an electron-microscopic photograph of a zeolite builder prepared by the process of this invention. From these Figures it will readily be understood that the builder prepared by the process of this invention has a remarkably fine primary particle size ( $<1 \mu$ ) and has excellent uniformity of the particle size.

In the builder prepared by the process of this invention, not only is the primary particle size remarkably fine, but also the effective particle size in practice, that is the secondary particle size, is remarkably fine, being smaller than  $4 \mu$ . The secondary particle size is preferably determined according to the following method for measurement of the particle size distribution.

(iii) Method for measurement of particle size distribution:

The measurement is preferably carried out by using an apparatus of the light scanning type for prompt measurement of the particle size distribution (model PSA-2 manufactured by Hitachi Seisakusho K.K.). Particles are suspended in a liquid, and the suspension is agitated to disperse the particles uniformly. Dispersed particles are sedimented with the lapse of time according to Stokes' law and the particle concentration distribution is generated in the liquid because of the difference of particle sizes. The particle size distribution is determined by utilising this principle. That is, the particle concentration distribution is optically measured after a certain period of time has passed from dispersing of the particles and is electrically recorded by converting optical signals to electric signals. Practical measurement procedures are as follows:

In a corked test tube (having a capacity of 10 ml) is charged 20 mg of a sample and 5 ml of a 0.1% solution of sodium hexametaphosphate is added. The corked test tube is attached to a shaking device and the content is shaken at a rate of about 60 reciprocations per minute for 30 minutes to disperse the sample in the sodium hexametaphosphate solution. The dispersion is transferred into a measurement cell (8.5 cm in height, 2.0 cm in length and 2.0 cm in width), and deionised water is poured until the liquid level reaches precisely a standard line (50 ml). The cell is then set to the measurement apparatus, and the content of the cell is sufficiently stirred by an agitation rod and is then allowed to stand still. Simultaneously with stopping of the agitation, a stopwatch is actuated. Then the apparatus is actuated to draw a particle size distribution curve and an approximate measurement time is examined. This opera-

tion is performed to know whether or not it is possible to obtain precise values. If de-ionised water has not been added precisely to the standard line, the top portion of the obtained curve is disturbed and precise values cannot be obtained. When it is confirmed by the above preliminary operation that a precise curve will be obtained, an automatic recorder is actuated to draw a particle size distribution curve. The measurement time and the density and viscosity of the liquid can conveniently be read in advance from a calibration table provided for the particular apparatus used. The recorded curve is divided in equal portions according to the so-calculated particle size and the intensity of transmitted light on the dividing point of the curve is read and  $\log I$  is then read from a logarithmic conversion scale. Based on the  $\log I$  value, the particle size distribution may be conveniently calculated from a prescribed calculating paper.

Since both the primary particle size and the secondary particle size are very fine, the finely divided zeolite prepared by the process of this invention has excellent water-dispersibility and shows a very high suspension stability when it is actually used for washing in a detergent composition. The water-dispersibility can be evaluated as described in the aforementioned Application No. 47950/76 (Serial No. 1 571 003).

#### Acid Treatment of Smectite Clay Mineral

In the preparation of the zeolite builder by the process of this invention, a smectite clay mineral is first subjected to the acid treatment to prepare activated silica or activated alumina-silica under such conditions that at least the X-ray diffraction peak of the plane index [001] is reduced to less than 15% of its original height.

In this invention, as the smectite clay mineral, there can be used, for example, montmorillonite clay minerals (so-called acid clays), bentonite, sub-bentonite and Fuller's earth, and beidellite, saponite and nontronite. These clay minerals may be used singly or in the form of a mixture of two or more of them. Further, these clay minerals may be used in the form of mixtures with other clay type minerals. Moreover, naturally modified smectite clay minerals, for example, a clay having a slightly destroyed smectite multi-layer structure, which is produced at Sanko, Shibata city, Niigata prefecture, Japan, may also be used in this invention.

In general, a smectite clay mineral has as the basic structure a three-layer structure comprising a central octahedral layer sandwiched between two tetrahedral layers of  $\text{SiO}_2$ , and a great number of these basic three-layer structures are laminated in the direction of the axis C to form a multi-layer

crystal structure inherent of the smectite clay mineral. The acid treatment is carried out under such conditions that this multi-layer crystal structure is substantially destroyed; i.e. the X-ray diffraction peak of the plane index [001] is reduced as aforesaid. By this acid treatment, it is made possible to obtain a zeolite having the desirable properties of a high calcium ion binding ability (described in the aforesaid Application No. 47950/76) (Serial No. 1 571 003) and a very fine primary particle size.

Figure 3 illustrates an X-ray diffraction pattern of acid clay produced at Nakajo, Niigata prefecture, Japan, and Figure 4 illustrates an X-ray diffraction pattern of alumina-silica treated under conditions 5-2 of Example 5 given hereinafter, in which destruction of the multi-layer crystal structure by the acid treatment is insufficient. Figures 5 and 6 illustrate X-ray diffraction patterns of alumina-silica obtained in Example 5 hereinafter, in which the multi-layer crystal structure is completely destroyed by the acid treatment. In samples shown in Figures 3 and 4, the X-ray diffraction peak of the plane index [001] is clearly left, but in samples shown in Figures 5 and 6, the X-ray diffraction peak of the plane index [001] substantially disappears.

From results obtained in Example 5 given hereinafter, it will readily be understood that destruction of the multi-layer crystal structure is important for obtaining a zeolite having an excellent calcium ion binding ability and a very fine primary particle size. For example, if there is employed acid clay *per se* having an X-ray diffraction pattern shown in Figure 3 or aluminosilica in which destruction of the multi-layer crystal structure is insufficient, such as sample 5-2 shown in Figure 4 and Table 12 given hereinafter, crystallisation to a zeolitic structure is insufficient and properties of the builder, such as the calcium ion binding ability, are degraded. Further, in such case, the primary particle size is larger than  $1 \mu$  and the intended objects of this invention cannot be attained. In contrast, when alumina-silicas having X-ray diffraction patterns as shown in Figures 5 and 6 are used, which have been acid-treated according to this invention, higher crystallisation to a zeolitic structure can be attained under the same zeolite-forming conditions and excellent builder characteristics can be obtained. Moreover, a builder having a very fine primary particle size can be obtained.

In this invention, in order to obtain a zeolite builder having a very fine primary particle size and preferred characteristics, it is essential for the activated silica or alumina-silica obtained by the acid treatment to have a degree of the crystal destruction (D.C.) as indicated by the peak of the plane index [001] lower than 15%, especially lower than

5%, as measured according to the method described below.

(iv) Method for determination of degree of crystal destruction (D.C.):

5 X-ray diffraction patterns of the starting raw clay mineral and acid-treated clay mineral are obtained according to the method for determining X-ray diffraction patterns, which has been described in (i) above.

10 With respect to each of the X-ray diffraction patterns of the starting and acid-treated clays, the respective heights of the peak of the plane index [001] and of index [110]

and [020] are measured. When the measurement is carried out under conditions specified herein, the peak of the plane index [001] appears at 4 to 7°, differing to some extent depending on the kind of the clay, and a single peak of the plane indexes [110] and [020] appears at 19.6 to 19.9°. [001] D.C. and [020] D.C. values (%) are calculated according to the formula given below and the total degree of crystal destruction caused by the acid treatment is evaluated based on these values.

$$[001] \text{ D.C. (\%)} = \frac{\text{(peak height of plane index [001] of acid-treated clay)}}{\text{(peak height of plane index [001] of starting raw clay)}} \times 100$$

$$[020] \text{ D.C. (\%)} = \frac{\text{(peak height of plane indexes [110] and [020] of acid-treated clay)}}{\text{(peak height of plane indexes [110] and [020] of starting clay)}} \times 100$$

30 In this invention, in order to obtain a zeolite builder having a finest primary particle size and optimum builder characteristics, it is preferred that the acid treatment be carried out under such conditions that the value of [020] D.C. (as well as that of [001] D.C.) is lower than 15%, preferably lower than 5%; i.e. even the basic three-layer structure of the starting clay is substantially destroyed.

35 The acid treatment of the smectite clay mineral can be performed by known methods, so far as the above-mentioned requirement is satisfied. As the acid, there can be used, for example, mineral acids such as sulphuric acid, hydrochloric acid and nitric acid, and organic acids such as benzene-sulphonic acid, toluene-sulphonic acid and acetic acid. However, a mineral acid such as sulphuric acid is ordinarily used. The contact of the clay with the acid may be performed according to known methods, and methods for the acid treatment of clays, which were previously proposed by us, can be effectively and preferably adopted (see Japanese Patent Publications Nos. 5666/53, 112/54, 2169/54, 2960/57, 11208/70, 11209/70, 44154/72, etc.). For example, the so-called slurry activation method in which a clay is contacted with an acid in the slurry state, the so-called granule activation method in which a granulated clay is subjected to solid-liquid contact with an acid and the so-called dry activation method in which a mixture of a clay and an acid is reacted in the dry state (in the granulated form) and then, the resulting salts are extracted may be adopted for accomplishing the acid treatment of this invention.

70 The concentration of the acid used for the acid treatment, the treatment and the treatment time are changed depending on the kind of the clay mineral and the treatment method, and it is difficult to specify these conditions. For example, when the acid treatment is performed according to the dry method, a smectite clay mineral such as mentioned above is intimately contacted with 0.3 to 1.5 equivalents, especially 0.5 to 1.2 equivalents, based on the basic component in the clay, of an acid as it is or in the form of an aqueous solution in such a proportion that the amount of the acid or its aqueous solution is 0.5 to 1.2 parts by weight per part by weight of the clay on the dry basis, to thereby form directly a plastic or solid reaction product and this reaction product is treated in an aqueous medium at a pH lower than 1 to remove the basic metal component in the reaction product by extraction. The basic metal component referred to includes all the basic components contained in the clay, such as alkali metal, alkaline earth metal, iron and aluminium components. When the mixing ratio of the clay and the acid or its aqueous solution is maintained in the above-mentioned range, a solid or creamy admixture is formed. This admixture is maintained at 60 to 300°C for 10 to 600 minutes under such conditions that the X-ray diffraction peak of the plane index [001] substantially disappears, whereby the reaction is completed. Then, soluble basic components in the reaction product are extracted and removed by treating the reaction mixture in an aqueous medium having a pH lower than 1, preferably a pH lower than 0.5. In order to prevent hydrolysis of the soluble

basic components, it is important that the removal and extraction of the basic components should be performed under the above-mentioned pH conditions. If colloidal iron components formed by hydrolysis are included in the resulting activated alumina-silica, there is often observed a tendency that the yield of the resulting synthetic zeolite or the degree of crystallisation is considerably reduced.

When activated alumina-silica is prepared by the acid treatment by solid-liquid contact of a granulated clay and a mineral acid, the mineral acid having a concentration of 10 to 98% is added to the clay in an amount of 0.01 to 0.1 part by weight per part by weight of the clay on the dry basis and the mixture is granulated to form a granular product which will not be disintegrated under conditions of the subsequent acid treatment. This non-disintegratable granulated clay is immersed in an aqueous solution of a mineral acid having a concentration of 5 to 72%, especially 10 to 50%, at a temperature in the range of from room temperature to the boiling point of the acid solution for 0.5 to 100 hours so that the X-ray diffraction peak of the plane index [001] substantially disappears.

The acid treatment of the clay mineral can also be accomplished according to the wet method in which the clay is dispersed in a mineral acid such as sulphuric acid having a concentration of 5 to 98%, and the clay is treated in the slurry state. In this case, the acid treatment conditions may be the same as those adopted in the above-mentioned acid treatment for the granulated clay.

In this invention, activated silica or activated alumina-silica is thus formed according to the degree of the acid treatment. This product has much higher activities, especially a much higher surface activity, than the untreated clay mineral or a product acid-treated under conditions outside the range specified in this invention. Preferably the activated silica or alumina-silica intermediate that is used in this invention has an aromatic adsorption index (AAI) of at least 16, more preferably 20 to 60, as measured according to the method described below. In view of the fact that untreated clay minerals have, in general, an AAI value lower than 15, it will readily be understood that the activated silica or alumina-silica formed by the above-mentioned acid treatment has a remarkably high surface activity. It is believed that because of this high surface activity, a synthetic zeolite for a detergent builder which has a very fine primary particle size and an excellent crystallinity can be obtained from this intermediate according to this invention.

(v) Method for determination of AAI values:

A sample which has been appropriately

pulverised in a mortar in advance is charged in a plugged weighing bottle having a suitable capacity, and the bottle is allowed to stand still for 3 hours in a drier maintained at  $150 \pm 5^\circ\text{C}$  and then placed in a desiccator. The content is thus cooled to room temperature naturally to form a test sample.

In a clean test tube for a centrifuge is charged  $1 \pm 0.005$  g of the test sample, and  $2 \pm 0.05$  cc of a liquid mixture comprising 30 parts by volume of anhydrous toluene and 70 parts by volume of anhydrous isooctane is added to the test sample by using a microburet. Then, the test tube is plugged and is shaken with a shaking angle of about  $60^\circ$  from the vertical line while the head of the tube is being lightly pressed, to thereby disperse the sample sufficiently in the liquid.

A rubber cap is set on the head portion of the test tube so as to prevent falling-out of the plug of the tube, and the test tube is attached to a shaking machine and shaken at a rate of 100 reciprocations per minute. Then, the test tube is subjected to an action of a centrifuge to form a supernatant. Refractive indexes of the obtained supernatant and the starting liquid mixture are measured by Abbé's refractometer, and the AAI value (the aromatic adsorption index) is calculated according to the following formula:

Aromatic adsorption index

$$(\text{AAI}) = [(n_D^{20})_1 - (n_D^{20})_2] \times 10^4$$

wherein  $(n_D^{20})_1$  denotes the refractive index of the liquid mixture comprising 30 parts by volume of toluene and 70 parts by volume of isooctane, and  $(n_D^{20})_2$  represents the refractive index of the supernatant.

#### Alkali Pre-Treatment

One of the important features of this invention resides in the novel finding that when the activated silica or activated aluminosilica obtained by the acid treatment of a smectite clay mineral is treated with an alkali hydroxide or a water-soluble alkali metal silicate (prior to the synthesis of the intended zeolite) to form an alkali metal polysilicate or alkali metal polyaluminosilicate having a composition in which the  $\text{Na}_2\text{O}/\text{SiO}_2$  molar ratio is in the range of from 1/3.5 to 1/500, preferably from 1/4 to 1/400, especially preferably from 1/7 to 1/300, a zeolite having an extremely fine particle size and excellent builder characteristics can be obtained.

In contrast, as shown in sample H—3 of Example 1 given hereinafter, if activated silica obtained by the acid treatment of a smectite clay mineral is directly mixed with aluminium and alkali metal components and water for zeolite crystallisation, the resulting zeolite has a primary particle size larger than  $1 \mu$  and has insufficient water dispersibility and rinsing property. Further, as shown in

sample H—4 of Example 2, even if an alkali hydroxide is added to the activated silica before mixing with the other components for zeolite crystallisation, the resulting zeolite still has a primary particle size considerably larger than  $1\ \mu$  and has less than excellent water dispersibility and rinsing property if the silica-alkali mixture has a composition similar to that of commercial water glass, rather than that specified above for the present invention.

The reason why a primary particle size smaller than  $1\ \mu$  can be obtained by this invention is not fully understood, but is thought to involve the presence of a great number of crystal nuclei in the zeolite crystallisation system, possibly due to a very high nucleus-forming speed combined with a relatively low crystal-forming speed, when the silica-alkali intermediate has the above specified composition. The multi-layer crystal structure of the smectite clay mineral, preferably together with the basic three-layer structure, is destroyed by the acid treatment, and is believed that by the specified alkali intermediate treatment the tetrahedral layer composed of  $\text{SiO}_2$  is combined with the alkali and provides promptly a great number of crystal nuclei for the zeolite crystallisation.

The pre-treatment of the acid-treated clay with an alkali metal hydroxide or a water-soluble alkali metal silicate may be accomplished by any convenient method, provided that the above-mentioned  $\text{Na}_2\text{O}/\text{SiO}_2$  molar ratio requirement is satisfied and both the components are intimately contacted with each other. In order to attain an intimate contact between both the components, it is preferred that both the components be contacted in the presence of water in an amount of 1 to 49 parts by weight, especially 2 to 19 parts by weight, per part by weight of the acid-treated clay. This water may be mixed with either the acid-treated clay or the alkali metal hydroxide or water-soluble alkali metal silicate or both, it being preferred that an aqueous slurry of the acid-treated clay be mixed with an aqueous solution of the alkali metal hydroxide or water-soluble alkali metal silicate.

Since the acid-treated clay *per se* has a high activity, good results are obtained even when the alkali treatment is carried out at room temperature, but if desired, the temperature may be elevated to about  $70^\circ\text{C}$ . A preferred treatment temperature is in the range of from room temperature to the boiling point of the mixture, especially from  $20$  to  $95^\circ\text{C}$ . The time for aging the mixture of both the components is changed depending on the temperature, but in general, the pre-treatment is carried out for 0.2 to 100 hours, especially 2 to 50 hours.

The alkali treatment may be performed under atmospheric pressure, but if desired,

can be conducted under heating at a pressure of up to about 5 atmospheres (gauge) in an autoclave or other sealed vessel. It also is possible to perform the treatment in a drying atmosphere. In this case, the treatment can be completed while drying the mixture of the acid-treated clay and alkali component. When the mixture of the acid-treated clay and alkali component is in a pasty or plastic state, the mixture may be moulded into granules, and the granules may be steamed in a water vapour atmosphere and dried or heated, whereby the intended treatment is accomplished.

#### Adjustment of Particle Size

In order to obtain a finely divided zeolite in this invention, it is preferred that the particle size of the alkali metal polysilicate or alkali metal polyaluminosilicate to be used for the zeolite-crystallisation be adjusted so that particles having a size smaller than  $5\ \mu$  occupy at least 20% by weight, preferably 50% by weight, of the total particles and particles having a size larger than  $20\ \mu$  occupy less than 30% by weight, preferably less than 10% by weight, of the total particles.

This particle size adjustment may be performed before the acid treatment, during the acid treatment, after the acid treatment (before the intermediate alkali treatment), during the intermediate alkali treatment or after that alkali treatment. If desired, it is possible to perform this particle size adjustment in two or more stages, for example, during the acid treatment and during the alkali treatment. For example, when the starting clay to be subjected to the acid treatment is subjected to one or more of dry and wet pulverising operations and classifying operations using a hydraulic elutriation, an air elutriation, a liquid cyclone, or a fluidised bed, the particle size of the raw material for the alkali metal polysilicate or polyaluminosilicate can be adjusted as required. When the particle size adjustment is thus made on the starting clay, impurities such as stone and sand contained in the raw clay mineral are effectively removed and a silica or aluminosilica intermediate having an enhanced reactivity can be obtained. Therefore, in this invention, there is advantageously adopted, for example, a method in which a fluidising gas is blown into an as-produced starting smectite clay mineral under agitation to separate the raw material into an upper fluidised layer of fine clay particles and a lower fixed or slightly fluidised layer of coarse particles containing stone, sand and other impurities.

Further, an alkali metal polysilicate or alkali metal polyaluminosilicate intermediate for the synthesis of the finely divided zeolite, which has the above-mentioned particle size distribution, can be obtained by wet-pulverising an acid-treated clay (acid-washed clay)

or an alkali-treated product in a pulveriser such as a ball mill, a tube mill, a mixer, an attritor, or a shaking mill and, if necessary, classifying the resulting particles by a liquid cyclone or other means.

Of course, it is possible to perform the particle size adjustment simultaneously with the acid treatment or the alkali treatment. In this case, a slurry of the starting clay and an acid or a slurry of the acid-treated clay and an alkali is preferably treated in a pulveriser such as a ball mill or a mixer or a highly shearing agitator. The slurry is passed through a classifying machine such as a liquid cyclone during the acid or alkali treatment or after the acid or alkali treatment to collect particles having a desirable size. By any of the foregoing particle size adjustment treatments, an intermediate having the above-mentioned desirable particle size distribution can be obtained.

If necessary, such treatments as water washing and drying may be performed before or after the acid treatment, the alkali treatment and the particle size adjustment. The alkali metal polysilicate or polyaluminosilicate intermediate, which has been subjected to the above-mentioned treatments, is used for the synthesis of the intended zeolite in an optional form, for example, a dry powder, a cake or a slurry.

#### Preparation of Homogeneous Mixture

According to the process of this invention, the above-mentioned finely divided alkali metal polysilicate or polyaluminosilicate is mixed with additional amounts of alumina and alkali metal components and water and the mixture is aged if necessary to form a homogeneous mixture having the specified composition capable of forming zeolite of the type A.

As the alumina component, there can be used, for example, fine powders of amorphous alumina such as hydrogel and xerogel of aluminium hydroxide, alumina monohydrate such as boehmite and pseudo-boehmite, alumina trihydrate such as bayerite, gibbsite and nordstrandite, and active alumina such as  $\gamma$ -alumina,  $\eta$ -alumina,  $\delta$ -alumina,  $\kappa$ -alumina,  $\theta$ -alumina, and  $\chi$ -alumina. As the alkali metal component, there can be preferably employed alkali metal hydroxides such as sodium hydroxide, potassium hydroxide and lithium hydroxide. The alumina and alkali metal components may be used in the

form of a compound or mixture of both the components. Use of an alkali metal aluminate is especially preferred. When an alkali metal aluminate is employed, if an excessive amount of the alumina or alkali metal components is necessary, such component is fed to the reaction system in the alkali metal aluminate.

In known processes for production of zeolite of the type A, zeolite-forming components are present in the crystallisation mixture in the following ratios (based on the oxides):

	Ordinary Range	Preferred Range
$\text{SiO}_2/\text{Al}_2\text{O}_3$	0.06— 5	0.1— 3.5
$\text{Na}_2\text{O}/\text{SiO}_2$	0.3 — 18	0.5— 5
$\text{H}_2\text{O}/\text{Na}_2\text{O}$	4 —300	15 —150

The advantageous product of the present invention is achieved by the use of the same mixing ratios in the crystallisation mixture, but with the specified  $\text{Na}_2\text{O}/\text{SiO}_2$  ratio in the intermediate which is incorporated in the crystallisation mixture.

It is preferred to avoid direct addition of an alkali metal hydroxide to the alkali metal polysilicate or alkali metal polyaluminosilicate in such an amount as will solubilise the intermediate. When this intermediate is directly mixed with a large amount of an alkali metal hydroxide, a zeolite having a coarse particle size tends to crystallise out, and this tendency is especially conspicuous when a water-soluble alkali metal silicate is used as the silica component. Accordingly, it is preferred that an alkaline aqueous solution of an alkali metal aluminate be gradually added to an aqueous dispersion of the alkali metal polysilicate or alkali metal polyaluminosilicate. Of course, an aqueous dispersion of the alkali metal polysilicate or alkali metal polyaluminosilicate and a solution of an alkali metal aluminate may be added continuously or intermittently into water simultaneously or alternately.

Since a solid silicate or aluminosilicate intermediate is used for the synthesis of zeolite, there is an optimum alkali concentration in the crystallisation mixture for obtaining a zeolite having a high degree of crystallisation and a fine particle size. It is preferred that the alkali concentration (CA, mole %), defined by the following formula, be in the range of from 7 to 0.25 mole %, especially from 5 to 0.5 mole %:

$$\text{CA (mole \%)} = \frac{[\text{Na}_2\text{O}]}{[\text{SiO}_2] + [\text{Al}_2\text{O}_3] + [\text{Na}_2\text{O}] + [\text{H}_2\text{O}]} \times 100$$

wherein  $[\text{SiO}_2]$ ,  $[\text{Al}_2\text{O}_3]$ ,  $[\text{Na}_2\text{O}]$  and  $[\text{H}_2\text{O}]$  represent mole numbers of  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Na}_2\text{O}$  and  $\text{H}_2\text{O}$ , respectively, in the mixture.

Moreover, in order to prepare a zeolite especially suitable as a detergent builder, it is desirable to control formation of sodalite hydrate effectively, for which purpose it is



preferred that the alkali concentration satisfy the following empirical formulae:

$$24 \geq t \cdot \exp \left[ 1.3 \times 10^4 \left( \frac{1}{363} - \frac{1}{T} \right) \right] \geq 0.5 \quad (1)$$

and

$$6 - 0.12 T \cdot \exp \left[ 1.3 \times 10^4 \left( \frac{1}{363} - \frac{1}{T} \right) \right] \geq CA \quad (2)$$

wherein  $t$  stands for the crystallisation time (hr),  $T$  stands for the crystallisation temperature ( $^{\circ}\text{K}$ , absolute temperature), and  $CA$  stands for an alkali concentration (mole %) in the zeolite-forming homogeneous mixture.

When this alkali concentration is higher than 7 mole %, the tendency for crystallisation of sodalite hydrate is undesirably enhanced, though this tendency differs to some extent depending on the temperature or time for mixing the zeolite-forming components as described hereinafter. A sodalite hydrate-containing zeolite has inferior calcium ion binding ability and washing power is therefore low when it is used as a detergent builder. When the alkali concentration is lower than 0.25 mole %, the resulting zeolite tends to have coarser particles.

Incorporation of colloidal iron compounds such as colloidal iron hydroxide into the crystallisation mixture must be avoided as far as possible. In general, industrially available alkali metal aluminates contain about 100 to about 5000 ppm, based on the oxide, of colloidal iron. We have found that if such a commercially available alkali metal aluminate is used for the synthesis of zeolite, an undesirably long time is required for crystallisation and sodalite hydrate is formed, resulting in reduction of the calcium ion binding ability, as aforesaid. Also, the resulting zeolite is coloured reddish brown to an unacceptable extent. These difficulties can be overcome by diluting such commercially available alkali metal aluminate with water so that the concentration as  $\text{Al}_2\text{O}_3$  is 3 to 20% by weight, thus flocculating the colloidal iron compounds which may then be removed by filtration to reduce the concentration of colloidal iron to a level lower than 50 ppm (as  $\text{Fe}_2\text{O}_3$ ).

When a commercially available sodium silicate solution is mixed with a commercially available sodium aluminate solution, since the respective components are gelled and highly viscous, a heterogeneous gel is readily formed. In contrast, in this invention, by using the above-mentioned specific zeolite-forming materials and adopting the above-mentioned specific mixing method, an entirely homogeneous slurry can easily be obtained without such difficulty. This slurry may be aged under agitation, if desired. The aging temperature and time are not particularly critical, but in

general, it is preferred that the aging be carried out at 0 to  $50^{\circ}\text{C}$ , especially 10 to  $30^{\circ}\text{C}$ , for 0.1 to 100 hours, especially 1 to 20 hours.

#### Crystallisation of Synthetic Zeolite

The above-mentioned homogeneous mixture having a specific composition is heated to crystallise out a finely divided zeolite having a primary particle size smaller than  $1 \mu$ .

It is preferred to crystallise the zeolite particles from a slurry at a temperature of 60 to  $200^{\circ}\text{C}$ , especially 70 to  $100^{\circ}\text{C}$ , over a period of 0.1 to 500 hours, especially 0.5 to 50 hours. While it is possible to conduct the crystallisation under a pressure generated by the reaction or under pressurisation with an inert gas in an autoclave or other pressure vessel, this is not essential. The zeolite particles can be crystallised out under mild conditions.

Agitation conditions are not particularly critical to the crystallisation, an ordinary crystallising tank equipped with an ordinary agitator being convenient for the present purposes.

The so formed synthetic type A zeolite in the form of very fine particles can be used as a detergent builder either in the as-prepared slurry form or after it has been subjected to a known solid-liquid separation operation such as filtration or centrifugal separation and to water washing and drying.

The synthetic zeolite is preferably separated from the mother liquor in a state where it contains at least a part of the excess alkali included in the mother liquor, and an acid or acidic salt is preferably added to the so separated composition to neutralise the alkali so that the pH of a suspension of the composition is not lower than 9.0, whereby the zeolite buffer capacity (S) (described in detail in the aforementioned Application No. 47950/76) (Serial No. 1 571 003) can be remarkably improved. As such acid or acidic salt, there can be employed those having a pKa value of at least 2, especially at least 2.5, for example, phosphorus oxy acids such as phosphoric acid, phosphorous acid and metaphosphoric acid, acidic salts of these phosphorus oxy acids, inorganic acids such as carbonic acid, boric acid, monosodium borate and activated silica solutions, organic acids such as citric acid, oxalic acid, tartaric

acid, succinic acid, maleic acid, malonic acid, gluconic acid, itaconic acid, thioglycolic acid, ethylenediamine-tetraacetic acid, nitrilotriacetic acid, diglycolic acid, sulphoitaconic acid, trimelic acid, pyromellitic acid, polyacrylic acid, maleic anhydridemethyl vinyl ether copolymers and carboxymethyl cellulose, and acidic salts of these inorganic and organic acids.

10 When phosphoric acid or its acidic salt is used for neutralizing the excess alkali, by heating the resulting phosphate-containing zeolite at an elevated temperature, for example, 300°C or higher, the phosphate may be converted to a condensed phosphoric acid salt, for example, a pyrophosphate.

#### Use

20 The synthetic zeolite can be combined with various surface active agents for use as detergent compositions. As such surface active agent, there can be mentioned, for example, anionic surface active agents such as sodium salts of fatty acids, sodium salts of higher alcohol-sulphuric acid esters, sodium alkyl benzene-sulphonates, sodium salts of alkyl sulphates, alkylolamide sulphuric acid esters,  $\alpha$ -olefin sulphonates, sodium alkyl sulphonates, sodium alkyl naphthalene-sulphonates, sulphonated fatty acid esters, sulphonated heterocyclic compounds, sulphonated fatty acid amides, sodium dialkyl suphosuccinates, fatty acid-amino acid condensates and Turkey red oil; non-ionic surface active agents such as polyoxyethylene alkyl ethers, polyoxyethylene alkyl aryl ethers, polyethylene glycol fatty acid esters, polyoxyethylene fatty acid esters, polyoxyethylene fatty acid amide ethers, polyhydric alcohol fatty acid esters, polyoxyethylene polyhydric alcohol fatty acid esters and alkylolamides; and amphoteric surface active agents such as betaine type surface active agents, imidazoline type surface active agents, sulphonic acid type amphoteric surface active agents and alanine type amphoteric surface active agents. These surface active agents may be used singly or in the form of mixtures of two or more of them.

50 The so formed detergent compositions may further comprise one or more of other inorganic and organic builders according to the intended use. As the inorganic builder, there can be mentioned, for example, polysilicate builders, sodium silicate, sodium carbonate, sodium bicarbonate, sodium sesquicarbonate, sodium orthophosphate, sodium pyrophosphate, potassium pyrophosphate, sodium tripolyphosphate, sodium tetraphosphate, sodium hexametaphosphate, borax, sodium chloride and sodium borate. As the organic builder, there can be mentioned, for example, sodium citrate, sodium oxalate, carboxymethyl cellulose, sodium nitrilotriacetate, sodium diglycolate, sodium gluconate, sodium hydroxysuccinate, sodium mellitate, sodium

ethylenediamine-tetraacetate, sodium polymaleate, sodium polyitaconate, sodium polymesaconate, sodium polyfumarate, sodium polyaconitate, sodium polycitraconate, sodium polymethylenemalonate, sodium carboxymethoxymalonate, sodium carboxymethoxysuccinate, sodium cis-cyclohexane-hexacarboxylate, sodium cis-cyclopentane-tetracarboxylate and sodium phloroglucinol-trisulphonate.

These detergent compositions may further comprise known additives customarily used in this field, for example, bubble-controlling agents, fluorescent whitening agents, bluing agents, other colorants, perfumes and caking preventing agents.

The synthetic zeolite is preferably incorporated in a detergent composition in an amount of 0.1 to 95% by weight, especially 1 to 50% by weight, based on solids, depending on the intended use of the detergent.

By virtue of the above-mentioned various characteristic properties, the synthetic zeolite builder can be used effectively for powdery and granular detergents, especially household laundry detergents. Further, it must be noted that the foregoing various advantages of the synthetic zeolite can similarly be attained when it is used in various dry-cleaning detergents, liquid detergents, solid soaps, powdery soaps, washing powders, detergents for table wares, detergents for glass and tiles and detergents for automobiles.

Embodiments of this invention will now be described in detail by reference to the following Examples and Comparative Examples.

#### EXAMPLE 1.

This Example illustrates the preparation of a synthetic zeolite for detergent builders from acid clay produced in Nakajo, Niigata Prefecture, Japan, as the smectite clay mineral.

The acid clay produced in Nakajo, Niigata Prefecture, Japan, which was used in this Example, contained 45% by weight in the as-produced state, and the metallic oxide composition of the clay (based on the product dried at 110°C) was as follows:

SiO <sub>2</sub>	72.1	% by weight	
Al <sub>2</sub> O <sub>3</sub>	14.2	% by weight	115
Fe <sub>2</sub> O <sub>3</sub>	3.87	% by weight	
MgO	3.25	% by weight	
CaO	1.06	% by weight	
Ignition loss	3.15	% by weight	

120 The starting acid clay was moulded into columns having a diameter of 5 mm and a length of 5 to 20 mm, and 1250 Kg (as the dried product) of the moulded clay was charged in a lead-lined wood tank having a capacity of 5 m<sup>3</sup> and 3300 l. of sulphuric acid having a concentration of 47% by weight was added thereto. Then, the temperature

was elevated to 90°C and the acid treatment of the clay granules was carried out for 40 hours. Sulphates of basic components which had reacted with sulphuric acid were removed by decantation using a dilute solution of sulphuric acid and water, and the water washing was conducted until no sulphate ion was detected. Thus, a granular acid-treated product was obtained.

The degree of destruction of the crystal structure of the above granular acid-treated product was determined from the X-ray diffraction peaks. The granular acid-treated product was dried for 2 hours in a drier maintained at 110°C and the dried product was analysed. Obtained results are shown in Table 1. This acid-treated product will hereinafter be referred to as "activated silica" (having a water content of 50% by weight) (sample 1—1).

TABLE 1.  
Acid-Treated Product

Composition (% by weight)	Sample 1—1
Ignition loss	3.71
SiO <sub>2</sub>	94.26
Al <sub>2</sub> O <sub>3</sub>	1.27
Fe <sub>2</sub> O <sub>3</sub>	0.39
MgO	0.30
CaO	0.07
SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> Mole Ratio	126.2
AAI	38
[001] DC (%)	undetectable
[020] DC (%)	2

The above activated silica was wet-pulverised in a ball mill while adding water to adjust the concentration to 20% by weight, to obtain an activated silica slurry (sample 1—2) having a particle size distribution shown in Table 2 (as measured by particle size measurement device Model PSA—2 manufactured by Hitachi Seisakusho K.K.).

TABLE 2.  
Particle Size Distribution

	Sample 1—2
smaller than 5 $\mu$	46.0 %
5 to 20 $\mu$	54.0 %
larger than 20 $\mu$	0 %

A stainless steel vessel having a capacity of 2 m<sup>3</sup> was charged with 79.6 Kg of the slurry (sample 1—2) and 46.6 Kg of a commercially available caustic soda solution (containing 49% of NaOH) was added thereto. The mixture was agitated at 60°C for 6 hours to obtain an alkali metal polysilicate A having a composition corresponding to Na<sub>2</sub>O·8.8SiO<sub>2</sub>.

For comparison, in the same manner as described above, the same commercially available caustic soda solution was added to the above slurry (sample 1—2) at 20°C to obtain a slurry B having a composition corresponding

to Na<sub>2</sub>O·8.8SiO<sub>2</sub>, and the slurry was immediately used for the preparation of a synthetic zeolite without aging.

As one of the conditions for the preparation of a synthetic zeolite for detergent builders, the following composition (oxide mole ratios) was chosen.

$$\begin{aligned} \text{Na}_2\text{O}/\text{SiO}_2 &= 0.9 \\ \text{SiO}_2/\text{Al}_2\text{O}_3 &= 2.0 \\ \text{H}_2\text{O}/\text{Na}_2\text{O} &= 50.0 \\ \text{CA} &= 1.9\% \end{aligned}$$

An alkali metal aluminate solution having a composition of 18.54% of Na<sub>2</sub>O, 19.1% of Al<sub>2</sub>O<sub>3</sub>, and 62.4% of H<sub>2</sub>O and an Na<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> molar ratio of 1.6/1 was prepared by dissolving commercially available aluminium hydroxide in commercially available caustic soda. This aluminate solution was formed as the alkali metal aluminate solution to be added to the above alkali metal polysilicate A or B so as to attain the above composition (oxide mole ratios).

Process for preparation of synthetic zeolite for detergent builders:

Water was added to the alkali metal polysilicate slurry A or B to adjust the SiO<sub>2</sub> concentration to 10%, and the mixture was charged in a stainless steel vessel having a capacity of 3.5m<sup>3</sup>. A solution formed by adding water to the above alkali metal aluminate solution under agitation at 20°C to adjust Na<sub>2</sub>O and Al<sub>2</sub>O<sub>3</sub> concentrations to 12.5% and 12.8%, respectively, was added to the above mixture over a period of about 80 minutes. The mixture was once gelled and it was finally converted to a homogeneous slurry. Then, the mixture was heated at 95°C and reaction was carried out for 3 hours under agitation to form crystalline particles of a zeolite. Then, the reaction product was washed with water and filtered. The filter cake was recovered and dried in a drier maintained at 110°C to obtain a synthetic zeolite (sample 1—3 or sample H—1).

The so prepared zeolite sample 1—3 (derived from the alkali metal polysilicate slurry A) and zeolite sample H—1 (derived from the alkali metal polysilicate slurry B) were tested as described hereinbefore to determine the X-ray diffraction crystal form and the primary particle size (Dp), and other parameters as described in the aforementioned Application No. 47950/76 (Serial No. 1 571 003).

In addition to the sample H—1 prepared by using the non-aged alkali metal polysilicate B, commercially available zeolites A and B (samples H—2 and H—3) were similarly tested as comparative samples.

The crystal form was substantially the same as that of zeolite type A in each case, but only Sample 1—3 produced a primary particle size less than 1  $\mu$ , the observed values

being Sample 1—3: 0.4  $\mu$ ; Sample H—1: 1.1  $\mu$ ; Sample H—2: 2  $\mu$ ; Sample H—3: 3  $\mu$ . Other tests, and the chemical composition of the zeolite and use in a detergent composition are described in the aforementioned Application No. 47950/76 (Serial No. 1 571 003).

#### EXAMPLE 2.

This Example illustrates influences of the amount of the alkali metal hydroxide that is used for the pre-treatment of activated silica.

The activated silica slurry sample 1—2 prepared in Example 1 by acid-treating the clay mineral was treated with sodium hydroxide in the following manner.

Each of 10 glass beakers having a capacity of 1 litre was charged with 600 g of the activated silica slurry sample 1—2 obtained in Example 1. Sodium hydroxide (NaOH) was added into 9 beakers in amounts of 160 g, 54 g, 40 g, 32 g, 23 g, 16 g, 11 g, 8 g and 0.33 g, respectively, while no sodium hydroxide was added to the remaining one beaker. The treatment was conducted at 90°C under agitation to form alkali metal polysilicate compositions in which the  $\text{Na}_2\text{O}/\text{SiO}_2$  molar ratios were 1/1, 1/3, 1/4, 1/5, 1/7, 1/10, 1/15, 1/20 and 1/500, respectively.

The alkali metal polysilicate composition in which the  $\text{Na}_2\text{O}/\text{SiO}_2$  molar ratio was 1/1 was kept substantially in the solution state.

The activated silica slurry (no sodium hydroxide was added) and the so formed alkali metal polysilicate compositions were mixed with a solution of sodium aluminate (having an  $\text{Al}_2\text{O}_3$  concentration of 19.09% and an  $\text{Na}_2\text{O}$  concentration of 22.49%) and sodium hydroxide to form gelatinous slurries of sodium aluminosilicate. In each run, the composition was adjusted so that the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  molar ratio was 2.0 and the CA value was 1.62 mole %. Each slurry was reacted under heating at 90°C for 6 hours to crystallise out a synthetic zeolite.

There were thus obtained the following synthetic zeolites; namely sample H—4 (no sodium hydroxide was added), sample H—5 (the  $\text{Na}_2\text{O}/\text{SiO}_2$  molar ratio at the pre-treatment was 1/1), sample H—5A (the  $\text{Na}_2\text{O}/\text{SiO}_2$  molar ratio at the pre-treatment was 1/3) and samples 2—2, 2—3, 2—4, 2—5, 2—6, 2—7 and 2—8 (the  $\text{Na}_2\text{O}/\text{SiO}_2$  molar ratios at the pre-treatment were 1/4, 1/5, 1/7, 1/10, 1/15, 1/20 and 1/500, respectively).

Properties of the so obtained synthetic zeolites were determined in the same manner as described in Example 1, the crystal form being substantially that of type A zeolite in each case and the primary particle sizes (Dp) being:—

Sample	Dp $\mu$	
H—4	1.1	
H—5	2.3	
H—5A	1.0	65
2—2	0.9	
2—3	0.8	
2—4	0.8	
2—5	0.5	
2—6	0.4	70
2—7	0.4	
2—8	0.6	

Other tests and use of the zeolites in detergent compositions are described in the aforementioned Application No. 47950/76 (Serial No. 1 571 003).

#### EXAMPLE 3.

This Example illustrates influences of conditions of the pre-treatment of activated silica.

(A) To 600 g of the activated silica slurry sample 1—2 prepared in Example 1 was added 7.6 g of sodium hydroxide so that the  $\text{Na}_2\text{O}/\text{SiO}_2$  molar ratio was 1/21. The mixture was aged under agitation for 15 hours at  $20 \pm 2^\circ\text{C}$  to form an alkali metal polysilicate slurry. Then, sodium aluminate was added to the slurry so that the  $\text{Na}_2\text{O}/\text{SiO}_2$  molar ratio was 1.0, the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  molar ratio was 2.0 and the  $\text{H}_2\text{O}/\text{Na}_2\text{O}$  molar ratio was 60. Then, the resulting gelatinous slurry of sodium aluminosilicate was heated at 90°C to effect crystallisation and obtain a synthetic zeolite (sample 3—1).

(B) To 100 g of the activated silica sample 1—1 (having a water content of 50%) described in Example 1 was added 3.2 g of sodium hydroxide so that the  $\text{Na}_2\text{O}/\text{SiO}_2$  molar ratio was 1/21. The mixture was sufficiently kneaded in a mortar and dried in a drier maintained at 110°C. Then, water was added to the resulting alkali metal polysilicate so that the  $\text{SiO}_2$  concentration was 10% by weight, and the mixture was pulverised in a ball mill. Then, sodium aluminate was added to the resulting alkali metal polysilicate slurry so that the  $\text{Na}_2\text{O}/\text{SiO}_2$  molar ratio was 1.0, the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  molar ratio was 2.0 and the  $\text{H}_2\text{O}/\text{Na}_2\text{O}$  molar ratio was 60. The resulting gelatinous slurry of sodium aluminosilicate was heated at 90°C to effect crystallisation and obtain a synthetic zeolite (sample 3—2).

Physical properties of these zeolite samples 3—1 and 3—2 were determined in the same manner as described in Example 1, the crystal form being substantially the same as that of type A zeolite and the primary particle sizes being 0.4  $\mu$  for Sample 3—1 and 0.7  $\mu$  for Sample 3—2. Other tests and use in detergent compositions are described in the aforementioned Application No. 47950/76 (Serial No. 1 571 003).

## EXAMPLE 4.

This Example illustrates an embodiment comprising drying and pulverising activated silica obtained by acid-treatment of the clay, adding water to the resulting powder of activated silica to form a slurry, adding a commercially available sodium silicate solution to the slurry to effect the pre-treatment, adding a solution of sodium aluminate to the resulting sodium polysilicate and crystallising out a zeolite.

The sodium silicate solution was mixed with the activated silica slurry sample 1-2 prepared in Example 1 so that the  $\text{Na}_2\text{O}/\text{SiO}_2$  molar ratio in the resulting composition was 1/4, 1/6, 1/8, 1/10, 1/15, 1/20 or 1/500.

Then, a sodium aluminate solution having an  $\text{Al}_2\text{O}_3$  concentration of 19.09% and an  $\text{Na}_2\text{O}$  concentration of 22.49% was added together with water and sodium hydroxide to the above alkali polysilicate composition so that the  $\text{Na}_2\text{O}/\text{SiO}_2$  molar ratio was 1.32, the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  molar ratio was 1.94 and the  $\text{H}_2\text{O}/\text{Na}_2\text{O}$  molar ratio was 61.8. The resulting gelatinous slurry of sodium aluminosilicate was heated and reacted at 90°C for 6 hours to crystallise out a synthetic zeolite.

There were thus obtained synthetic zeolites; namely sample H-7A (the  $\text{Na}_2\text{O}/\text{SiO}_2$  molar ratio was 1/4 in the alkali polysilicate composition) and samples H-7B, 4-3, 4-4, 4-5, 4-6 and H-7C (the  $\text{Na}_2\text{O}/\text{SiO}_2$  molar ratios in the alkali polysilicates compositions were 1/6, 1/8, 1/10, 1/15, 1/20 and 1/500, respectively).

For comparison, in the same manner as described above, the above sodium aluminate solution was added to the sodium silicate solution and a synthetic zeolite (sample H-6) was prepared from the resulting sodium aluminosilicate gelatinous slurry.

Another comparative zeolite builder (sample H-7) was prepared according to the teaching of Japanese Patent Application Laid-Open Specification No. 12381/75 in the following manner:

Powder of activated silica was added to the sodium silicate solution to form sodium silicate having a composition corresponding to  $\text{Na}_2\text{O} \cdot 6\text{SiO}_2$ , and the sodium silicate was added together with water and sodium hydroxide to sodium aluminate so that the  $\text{Na}_2\text{O}/\text{SiO}_2$  molar ratio was 1.32, the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  molar ratio was 1.94 and the  $\text{H}_2\text{O}/\text{Na}_2\text{O}$  molar ratio was 61.8 in the resulting sodium aluminosilicate gel. Then, the mixture was agitated and blended at a rotation speed of 10000 to 12000 rpm by using an agitating mixer (Model VA-853 manu-

factured by Hitachi Seisakusho K.K.). The resulting sodium aluminosilicate gel slurry was heated and reacted at 80°C for 24 hours under agitation to form a synthetic zeolite (sample H-7).

Properties of these zeolites were determined in the same manner as described in Example 1 the crystal form being substantially the same as that of type A zeolite in each case, and the primary particle sizes (Dp) being:—

Sample	Dp ( $\mu$ )	
H-6	2.1	70
H-7	5.4	
H-7A	1.0	
H-7B	1.0	
H-7C	1.0	75
4-3	0.8	
4-4	0.6	
4-5	0.6	
4-6	0.7	

Other tests and use in detergent compositions are described in the aforementioned Application No. 47950/76 (Serial No. 1 571 003).

## EXAMPLE 5.

In this Example, the same acid clay as used in Example 1, that was produced in Nakajo, Niigata Prefecture, Japan, was treated with sulphuric acid under various conditions.

The starting acid clay was moulded in columns having a diameter of 5 mm and a length of 5 to 20 mm, and 76.5 g each of the moulded clay as calculated as the dried product was charged into four conical beakers having a capacity of 500 ml. Then, 200 ml of sulphuric acid having a concentration of 50% by weight was added to each beaker. Then, the granular clay was acid-treated at 90°C for 2, 8, 20 or 30 hours. Sulphates of basic components that had reacted with sulphuric acid were washed away and removed by decantation using dilute sulphuric acid and water. The recovered acid-treated clay was washed with water until sulphate ion was not detected at all. Thus, there were obtained 4 acid-treated clays. The starting acid clay was designated as sample 5-1, and products acid-treated for 2, 8, 20 and 30 hours were designated as samples 5-2, 5-3, 5-4 and 5-5, respectively.

These samples 5-1 to 5-5 were subjected to X-ray diffraction analysis and the degrees of crystallinity (DC, %) were determined from the diffraction peaks. Further, each sample was subjected to chemical analysis. Obtained results are shown in Table 3.

TABLE 3

	Sample 5—1	Sample 5—2	Sample 5—3	Sample 5—4	Sample 5—5
Acid Treatment Time (hours)	0(untreated)	2	8	20	30
X-Ray Diffraction Pattern	Fig. 3	Fig. 4	Fig. 5	Fig. 6	—
Composition (% by weight)					
ignition loss	5.27	5.5	5.6	3.11	3.60
SiO <sub>2</sub>	72.1	76.22	84.2	94.10	94.21
Al <sub>2</sub> O <sub>3</sub>	14.23	11.3	7.1	1.67	1.30
Fe <sub>2</sub> O <sub>3</sub>	3.87	3.18	1.4	0.46	0.43
MgO	3.47	2.8	1.2	0.31	0.31
CaO	1.06	1.0	0.5	0.07	0.15
SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> Molar Ratio	8.6	11.47	20.2	95.8	123.2
AAI	8	16	39	37	37
[001] DC (%)	100	18	undetectable	undetectable	undetectable
[020] DC (%)	100	80	15	5	3

5 The above granular acid-treated products were treated in order to attain a particle size distribution suitable for the production of an alkali polysilicate for the synthesis of a zeolite builder. More specifically, the untreated starting clay or acid-treated product was put into a household mixer (Mode VA—853 manufactured by Hitachi Seisakusho K.K.) and water was added thereto so that the solid concentration was 20% by weight, and the mixture was agitated and pulverised for 40

minutes and sieved by using a 270—Typer mesh sieve. Thus, a slurry of the untreated starting clay or acid-treated products having the particle size thus adjusted was obtained. The particle size distribution (% by weight) was determined to obtain results shown in Table 4. With respect to sample 5—4 as a typical instance, the secondary particle size distribution (Ds) was examined in more detail to obtain results shown in Table 5.

TABLE 4

Particle Size Distribution (% by weight)	Sample 5—1	Sample 5—2	Sample 5—3	Sample 5—4	Sample 5—5
0—5 $\mu$	65.4	65.1	64.8	65.0	64.9
5—20 $\mu$	34.6	34.9	35.2	35.0	35.1
above 20 $\mu$	0	0	0	0	0

TABLE 5

Secondary Particle Size Distribution (Ds) (% by weight)	Sample 5—4
0—1 $\mu$	4.6
1—2 $\mu$	10.3
2—3 $\mu$	19.2
3—4 $\mu$	20.1
4—5 $\mu$	10.8
5—6 $\mu$	10.5
6—7 $\mu$	9.8
7—8 $\mu$	7.5
8—9 $\mu$	7.2
9—10 $\mu$	0

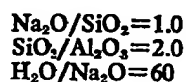
25 Then, 200 g each of samples 5—1 to 5—5 were charged into 1-litre capacity beakers, respectively, and 3 g, 3.2 g, 3.6 g, 4 g and 4 g

of sodium hydroxide were added to samples 5—1 to 5—5, respectively. Each mixture was aged at 60°C under agitation for 2 hours to

30

obtain an alkali metal polysilicate slurry.

As one of conditions for the synthesis of a synthetic zeolite, the following composition expressed in terms of oxide molar ratios was chosen:



being substantially the same as that of type A zeolite (plus Na for Sample H-9), and the primary particle size (Dp) being:

Sample	Dp ( $\mu$ )	
H-8	2.0	
H-9	1.5	
5-6	0.6	50
5-7	0.4	
5-8	0.3	

- 10 In order to attain the above molar ratios, necessary amounts of an alumina component and alkali metal and water components for the reaction were added to the above slurries of the acid-treated clays (the contents of SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> differed depending on the acid treatment conditions). More specifically, a commercially available sodium aluminate solution (having an Na<sub>2</sub>O content of 21.0% and an Al<sub>2</sub>O<sub>3</sub> content of 18.8%) was mixed with commercially available caustic soda (NaOH) and water so that the above composition was attained, and the mixture was filtered to obtain a purified liquid mixture. The acid-treated clay slurry and the resulting liquid mixture were charged in a beaker having a capacity of 2 litres so that the amount of the reaction mixture was about 1.5 litres. The mixture was agitated at 20°C, whereby the mixture once passed through a gelled state and was then converted to a homogeneous slurry. The temperature was elevated to 95°C and the mixture was agitated for 3 hours to effect reaction and form crystalline particles of a zeolite. The reaction mixture was filtered by a suction filter and washed with deionised water. The filter cake recovered was dried in a drier maintained at 110°C. Thus, there were obtained 5 synthetic zeolites, samples H-8, H-9, 5-6, 5-7 and 5-8, from the above samples 5-1 to 5-5, respectively.

Properties of the so obtained zeolites were determined in the same manner as described in Example 1, the crystal form in each case

Other tests and use in detergent compositions are described in the aforementioned Application No. 47950/76 (Serial No. 1 571 003).

#### EXAMPLE 6.

In this Example, as the starting smectite clay there were chosen (1) sub-bentonite produced in Tsugawa, Niigata Prefecture, Japan, (2) white clay produced in Sanko, Niigata Prefecture, Japan and (3) sub-bentonite produced in Chito, USA, they were acid-treated and synthetic zeolites were prepared from slurries of fine particles of the acid-treated clays.

To 500 g of the starting clay was added 9500 g of water, and the mixture was pulverised in a ball mill. The resulting slurry was subjected to classification and hydraulic elutriation by using a liquid cyclone to remove impurities and subjected to evaporation to adjust the water content to 50%. In a ball mill having a capacity of 7.5 litres, 325 g of concentrated sulphuric acid was added to the clay slurry to form a creamy mixture. The mixture was heated at 180°C in a steam atmosphere for 3 hours to effect the acid treatment. Sulphates formed by the reaction were washed away and removed, and the residue was washed with water until no sulphate ion was detected, to obtain an acid-treated clay.

Results of the chemical analysis and X-ray diffraction analysis of the starting clay and acid-treated clay are shown in Table 6.

TABLE 6

Clay	Sample 6-1 Sub-bentonite produced in Tsugawa, Niigata Prefecture, Japan		Sample 6-2 White clay produced in Sanku, Niigata Prefecture, Japan		Sample 6-3 Sub-bentonite produced in Chito, USA	
	Untreated	Acid-Treated	Untreated	Acid-Treated	Untreated	Acid-Treated
Composition (% by weight)						
ignition loss						
SiO <sub>2</sub>	3.65	4.3	11.85	8.5	7.14	6.91
Al <sub>2</sub> O <sub>3</sub>	73.96	88.31	53.11	83.49	60.37	86.01
Fe <sub>2</sub> O <sub>3</sub>	15.22	4.31	30.17	6.21	24.83	4.10
CaO	2.72	1.30	3.95	1.10	2.74	1.08
MgO	1.12	0.68	0.52	0.22	1.66	0.80
SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	2.42	1.1	1.31	0.48	3.22	1.10
Molar Ratio						
AAI	8.26	34.9	3.0	22.9	4.13	35.7
[001] DC (%)	2	24	7	33	1.5	40
[020] DC (%)	100	undetectable	100	undetectable	100	undetectable
	100	15	100	7	100	15

Water was added to each acid-treated product so that the solid concentration was 20% by weight, and the mixture was wet-pulverised in a ball mill to obtain a fine slurry. Each slurry was charged in a glass beaker having a capacity of 1 litre. Then, 9.7 g, 9.2 g and 9.5 g of sodium hydroxide were added to slurries of acid-treated products of samples 6-1, 6-2 and 6-3, respectively, under agitation, and each mixture was aged at 60°C for 2 hours to obtain an alkali metal polysilicate slurry, the Na<sub>2</sub>O/SiO<sub>2</sub> molar ratio being within the required range of 1:3.5 to 1:500 in all cases.

Then, alkali metal aluminosilicate crystallisation slurries were prepared from the above slurries in the same manner as described in

Example 1 while adjusting amounts added of sodium aluminate and NaOH based on the analysis values of the acid-treated products so as to attain the following composition in the crystallisation mixtures:—

Na<sub>2</sub>O/SiO<sub>2</sub> molar ratio=1.26  
SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio=2.0  
H<sub>2</sub>O/Na<sub>2</sub>O molar ratio=50

Then, in the same manner as described in Example 1, the crystallisation reaction was carried out using acid-treated clay samples 6-1, 6-2 and 6-3, respectively, and the reaction product Samples 6-5, 6-6 and 6-7 respectively were recovered by washing and drying. Properties of the so obtained



zeolites were determined in the same manner as described in Example 1 the crystal form being substantially the same as that of type A zeolite in each case, and the primary particle sizes being 0.8  $\mu$  for Sample 6—4, 0.7  $\mu$  for Sample 6—5, and 0.8  $\mu$  for Sample 6—6. Other tests and use in detergent compositions are described in the aforementioned Application No. 47950/76 (Serial No. 1 571 003).

#### EXAMPLE 7.

Water was added to 500 g of the same acid clay as used in Example 1, that was produced in Nakajo, Niigata Prefecture, Japan, to form 5 Kg of a mixture, and the mixture was sufficiently pulverised in a ball mill and subjected to classification and hydraulic elutriation by using a liquid cyclone. Water was removed from the resulting clay slurry (sample 7—1) by filtration and drying

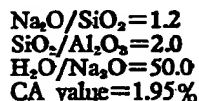
so that the water content was reduced to about 60%. The slurry was charged in a lead-lined vessel together with sulphuric acid having a concentration of about 40%, and the mixture was heated at 90°C under agitation for 20 hours to effect acid treatment, followed by filtration and water washing. Then, 13.4 g of sodium hydroxide was added to 100 g (as the dry product) of the so obtained activated silica (sample 7—2) at 60°C under agitation and the treatment was conducted for 2 hours to obtain an alkali metal polysilicate slurry (sample 7—3), in which the  $\text{Na}_2\text{O}/\text{SiO}_2$  molar ratio was within the required range of from 1:3.5 to 1:500.

Particle size distribution (Ds) of the clay slurry (sample 7—1), the activated silica slurry (sample 7—2) and the alkali metal polysilicate slurry (sample 7—3) are shown in Table 7.

TABLE 7

Particle Size Distribution (%)	Sample 7—1	Sample 7—2	Sample 7—3
0—5 $\mu$	70	78	84
5—20 $\mu$	30	22	16
above 20 $\mu$	0	0	0

A sodium aluminate solution and commercially available sodium hydroxide were added to the alkali metal polysilicate slurry so that the following composition (molar ratios) was attained in the crystallisation mixture:—



The so obtained alkali metal aluminosilicate gelatinous slurry was heated at 90°C to effect crystallisation reaction, and the reaction product (sample 7—4) was recovered through washing and drying. The crystal form of the reaction product was substantially that of type A zeolite, and its primary particle size was 0.3  $\mu$ . Other tests and use in detergent composition are described in the aforementioned Application No. 47950/76 (Serial No. 1 571 003).

#### EXAMPLE 8.

This Example illustrates another method for preparing alkali metal aluminosilicate gels. Run (A) (method comprising adding a slurry of an alkali metal polysilicate corresponding to  $\text{Na}_2\text{O} \cdot 10\text{SiO}_2$  to an alkali metal aluminate solution):

A beaker having a capacity of 2 litres was charged with 1118 g of an alkali metal aluminate solution containing 7.4% of  $\text{Al}_2\text{O}_3$  and 7.27% of  $\text{Na}_2\text{O}$ . Water was added to the same alkali metal polysilicate slurry as pre-

pared in Example 1 so that the  $\text{SiO}_2$  concentration was 10%, and 952 g of the resulting slurry was added to the above alkali metal aluminate solution over a period of about 30 minutes. The mixture was treated in the same manner as in Example 1 to obtain a homogeneous gelatinous slurry of an alkali metal aluminosilicate.

This alkali metal aluminosilicate slurry was reacted at 85°C for 4 hours to crystallise out a synthetic zeolite. The resulting crystal was recovered by filtration, washed with water and dried to obtain a synthetic zeolite (sample 8—1). Run (B) (method comprising simultaneously adding an alkali metal aluminate solution and an alkali metal polysilicate to water):

A beaker having a capacity of 2 litres was charged with 265 g of water, and 892 g of a slurry of an alkali metal polysilicate obtained as in Example 1 (corresponding to  $\text{Na}_2\text{O} \cdot 10\text{SiO}_2$ ) having an  $\text{SiO}_2$  concentration of 11.2% by weight and 913 g of an alkali metal aluminate solution having an  $\text{Al}_2\text{O}_3$  concentration of 9.1% by weight were simultaneously added to the content of the beaker under agitation over a period of about 30 minutes. At the initial stage of the mixing operation, slight increase of the viscosity was observed, but both the components were well dispersed in the latter stage and a homogeneous gelatinous slurry was obtained.

In the same manner as in Run (A), the slurry was reacted at 85°C for 4 hours to effect crystallisation. The resulting crystal was recovered by filtration, washed with water

and dried to obtain a synthetic zeolite (sample 8—2).

- Both of these synthetic zeolites had a crystal form substantially the same as that of type A zeolite and a primary particle size of 0.4  $\mu$ . Other tests and use in detergent compositions are described in the aforementioned Application No. 47950/76 (Serial No. 1 571 003).

#### EXAMPLE 9.

- This Example illustrates influences of the alkali concentration of the zeolite-crystallising-out reaction between sodium aluminate and an alkali metal polysilicate formed by subjecting an acid-treated acid clay to the pretreatment with an alkali metal component.

- Each of 3 beakers having a capacity of 1 litre was charged with 300 g of an alkali metal polysilicate slurry prepared in the same manner as in Example 1, and sodium aluminate comprising 18.54% of  $\text{Na}_2\text{O}$ , 19.1% of  $\text{Al}_2\text{O}_3$ , and 62.36% of  $\text{H}_2\text{O}$  and commercially available sodium hydroxide were added to the slurry together with water if necessary, so that the alkali concentration, CA value, was 4, 2.5 and 1.2 mole %. The composition was adjusted so that the  $\text{Na}_2\text{O}/\text{SiO}_2$  molar ratio was 1.0 and the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  molar ratio was 2.0. The resulting alkali metal aluminosilicate gel was reacted at 95°C for 3 hours under agitation to form crystalline particles of a synthetic zeolite. The mother liquor was removed, and the residue was washed with water and filtered and the filter cake was recovered. Thus, there were obtained 3 synthetic zeolites, namely sample 9—1 (prepared from the raw material having a CA value of 4 mole %), sample 9—2 (prepared from the raw material having a CA value of 2.5 mole %) and sample 9—3 (prepared from the raw material having a CA value of 1.2 mole %). Properties of these zeolites were determined in the same manner as described in Example 1 the crystal form being substantially that of type A zeolite in each case and the primary particle size being 0.2  $\mu$  for Sample 9—1, 0.4  $\mu$  for Sample 9—2, and less than 1 micron for Sample 9—3. Other tests and use in detergent compositions are described in the aforementioned Application No. 47950/76 (Serial No. 1 571 003).

#### EXAMPLE 10.

- In this Example, a synthetic zeolite prepared from an alkali metal aluminosilicate slurry was separated from the mother liquor in such a state that a part of excessive sodium hydroxide contained in the mother liquor was incorporated in the zeolite and an acid or acidic salt was added to the so separated zeolite composition to effect neutralisation and obtain a synthetic zeolite builder composition.

As the alkali metal aluminosilicate builder containing the alkali metal component, there

were chosen the zeolite crystal-containing slurry prepared in Example 1 from which the mother liquor had not been separated by filtration (base S), the filter cake formed by removing the mother liquor from base S by filtration so that the solid content was 50% (base C) and the filter cake formed by washing base C with water one time (base F). Then, an acid or acidic salt shown in Table 8 was added to such alkali metal component-containing zeolite composition (base S, C or F) in an amount indicated in Table 8 (parts by weight per 100 parts by weight of the base as the dried product, and the mixture was sufficiently agitated and blended and dried at about 170°C by using a hot air drier to form an alkali metal aluminosilicate builder in which a part of the contained alkali metal hydroxide component was neutralised and combined with the alkali metal component contained. Thus, there were prepared 34 kinds of such alkali metal silicate binders (samples 10—1 to 10—34) as shown in Table 8.

For comparison, an acid (sulphuric acid) was added for neutralisation so that the pH was reduced below 9.0, and the mixture was treated in the same manner as described above to form comparative sample H—12.

Comparative samples were prepared directly from bases S and C in which an acid or acidic salt was not incorporated. More specifically, a powdery sample H—10 was prepared by concentrating entirely base S according to a customary method for concentrating and solidifying slurries, drying the concentrate at about 170°C and pulverising the resulting solid, and a powdery sample H—11 was prepared by drying base C at about 170°C and pulverising the dried product.

The primary particle size was 0.4  $\mu$  in every case, and crystal form was substantially the same as that of type A zeolite (4A) except for comparative Samples H—10 and H—11 which had a sodalite crystal form. Other tests and use in detergent compositions are described in the aforementioned Application No. 47950/76 (Serial No. 1 571 003).

TABLE 8

Sample No.	
10—1	base S+ $\text{H}_2\text{SO}_4$ (3 parts)
10—2	base S+ $\text{H}_3\text{BO}_3$ (6 parts)
10—3	base S+citric acid(3 parts)
10—4	base S+citric acid(6 parts)
10—5	base S+citric acid(10 parts)
10—6	base S+ $\text{H}_3\text{PO}_4$ (3 parts)
10—7	base S+ $\text{H}_3\text{PO}_4$ (6 parts)
10—8	base S+ $\text{H}_3\text{PO}_4$ (10 parts)
10—9	base S+polysilicic acid(3 parts)
H—10	base S
10—10	base C+citric acid(3 parts)
10—11	base C+citric acid(6 parts)
10—12	base C+citric acid(10 parts)
10—13	base C+ $\text{H}_3\text{PO}_4$ (3 parts)

TABLE 8 (continuation)

Sample No.	
10-14	base C+H <sub>3</sub> PO <sub>4</sub> (6 parts)
10-15	base C+polysilicic acid(3 parts)
H-11	base C
10-16	base F+citric acid(1 part)
10-17	base F+citric acid(3 parts)
10-18	base F+citric acid(5 parts)
10-19	base F+citric acid(7 parts)
10-20	base F+H <sub>3</sub> PO <sub>4</sub> (1 part)
10-21	base F+H <sub>3</sub> PO <sub>4</sub> (5 parts)
H-12	base F+H <sub>2</sub> SO <sub>4</sub> (1 part)
10-22	base F+H <sub>3</sub> PO <sub>4</sub> (1 part)+NaOH
10-23	base F+H <sub>3</sub> PO <sub>4</sub> (3 parts)+NaOH
10-24	base F+H <sub>3</sub> PO <sub>4</sub> (5 parts)+NaOH
10-25	base F+H <sub>3</sub> PO <sub>4</sub> (10 parts)+NaOH
10-26	base F+Na <sub>2</sub> HPO <sub>4</sub> (1 part)
10-27	base F+Na <sub>2</sub> HPO <sub>4</sub> (3 parts)
10-28	base F+Na <sub>2</sub> HPO <sub>4</sub> (4.8 parts)
10-29	base F+NaH <sub>2</sub> PO <sub>4</sub> (1 part)
10-30	base F+NaH <sub>2</sub> PO <sub>4</sub> (3 parts)
10-31	base F+NaH <sub>2</sub> PO <sub>4</sub> (4.8 parts)
10-32	base F+H <sub>3</sub> PO <sub>4</sub> (5 parts)+NaOH
10-33	base F+H <sub>3</sub> BO <sub>3</sub> (10 parts)+NaOH
10-34	base F+polysilicic acid(13 parts)

## EXAMPLE 11.

This Example illustrates a builder composition prepared by separating a synthetic zeolite crystallised out at the step of preparing an alkali metal aluminosilicate builder from the mother liquor in a state where a part of excessive sodium hydroxide contained in the mother liquor is included into the zeolite, adding phosphoric acid (H<sub>3</sub>PO<sub>4</sub>) to the recovered zeolite composition and drying and calcining the resulting mixture, and a builder composition prepared by washing the above zeolite separated from the mother liquor with water, adding disodium hydrogenphosphate (Na<sub>2</sub>HPO<sub>4</sub>) to the washed zeolite and drying and calcining the resulting mixture.

## Run (A):

A 5% solution of commercially available phosphoric acid was added to base C described in Example 10 so that the pH was reduced to 10, and the resulting slurry composition was dried in a drier maintained at 110°C calcined at 500°C for 1 hour in an electric furnace and pulverised to obtain a powdery sample (sample 11-1).

## Run (B):

To 100 g of base F described in Example 10 was added a 10% solution of disodium hydrogen phosphate in an amount, as Na<sub>2</sub>HPO<sub>4</sub>, corresponding to 10% by weight based on the zeolite, and the mixture was dried in a drier maintained at 110°C, calcined at 500°C for 1 hour in an electric furnace and pulverised to obtain a powdery sample (sample 11-2).

Both samples had a crystal form substantially the same as that of type A zeolite (plus sodium phosphate) and a primary particle size of 0.4 μ. Other tests and use in detergent compositions are described in the aforementioned Application No. 47950/76 (Serial No. 1 571 003).

## WHAT WE CLAIM IS:—

1. A process for the preparation of detergent builders which comprises acid-treating a smectite clay mineral to prepare activated silica or activated alumina-silica under such acid-treating conditions that at least the X-ray diffraction peak of the plane index [001] is reduced to less than 15% of its original height, treating the resulting activated silica or activated alumina-silica with an alkali metal hydroxide or a water-soluble alkali metal silicate to prepare an alkali metal polysilicate or alkali metal polyaluminosilicate having a composition in which the Na<sub>2</sub>O/SiO<sub>2</sub> molar ratio is in the range of from 1/3.5 to 1/500, mixing said alkali metal polysilicate or alkali metal polyaluminosilicate with alumina and alkali metal components and water to prepare a homogeneous mixture having a composition capable of forming zeolite of the type A, and heating said homogeneous mixture to crystallise out fine particles of synthetic type A zeolite (as hereinbefore defined) having a primary particle size (as hereinbefore defined) smaller than 1 μ.

2. A process according to claim 1, wherein the smectite clay mineral is a montmorillonite clay mineral.

3. A process according to claim 1 or 2, wherein the smectite clay mineral is acid-treated so that the height of the X-ray diffraction peak of the plane index [001] of the acid-treated clay is reduced to less than 5%, of its original height.

4. A process according to claim 1, 2 or 3, wherein the smectite clay mineral is acid-treated so that the height of the X-ray diffraction peak of the plane index [110] [020] of the acid-treated clay is reduced to less than 15% of its original height.

5. A process according to claim 4, wherein the height of the X-ray diffraction peak of the plane index [110] [020] is reduced to less than 5% of its original height.

6. A process according to any of the preceding claims, wherein the smectite clay mineral is acid-treated so that the acid-treated clay has an aromatic adsorption index [AAI] of at least 16.

7. A process according to claim 6, wherein the clay is treated so that the said AAI is within the range from 20 to 60.

8. A process according to any of the preceding claims, wherein the said alkali metal polysilicate or alkali metal polyaluminosilicate has a composition in which the Na<sub>2</sub>O/SiO<sub>2</sub>

molar ratio is in the range of from 1/4 to 1/400.

9. A process according to claim 8, wherein the said  $\text{Na}_2\text{O}/\text{SiO}_2$  molar ratio is within the range from 1/7 to 1/300.

10. A process according to any of the preceding claims, wherein the activated silica or activated alumina-silica is treated with the alkali metal hydroxide or water-soluble alkali metal silicate in the presence of water in an amount of 1 to 49 parts by weight per part by weight of said activated silica or activated alumina-silica.

11. A process according to claim 10, wherein the said amount of water is 2 to 19 parts by weight.

12. A process according to any of the preceding claims, wherein an aqueous mixture of the activated silica or activated alumina-silica and the alkali metal hydroxide or water-soluble alkali metal silicate is aged for at least 0.2 hour.

13. A process according to claim 12, wherein the aqueous mixture is aged for at least 2 hours.

14. A process according to any of the preceding claims, wherein the particle size of the alkali metal polysilicate or alkali metal polyaluminosilicate is adjusted so that particles having a size smaller than  $5 \mu$  constitute at least 20% by weight of the total and particles having a particle size larger than  $20 \mu$  constitute less than 30% by weight of the total.

15. A process according to claim 14, wherein the particles smaller than  $5 \mu$  constitute at least 50% by weight of the total

and the particles larger than  $20 \mu$  constitute less than 10% by weight of the total.

16. A process according to claim 14 or 15, wherein the particle size adjustment is carried out in one or more stages before or during the acid treatment, or before, during or after the first alkali treatment.

17. A process according to any of the preceding claims, wherein the homogeneous mixture of the alkali metal polysilicate or alkali metal aluminosilicate with the alumina and alkali metal components has a composition in which the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  molar ratio is in the range of from 0.1 to 3.5, the  $\text{Na}_2\text{O}/\text{SiO}_2$  molar ratio is in the range of from 0.5 to 5, and the  $\text{H}_2\text{O}/\text{Na}_2\text{O}$  molar ratio is in the range of from 15 to 150.

18. A process according to any of the preceding claims, wherein the said homogeneous mixture is formed by adding an alkaline aqueous solution of an alkali metal alumininate to an aqueous dispersion of the alkali metal polysilicate or alkali metal polyaluminosilicate.

19. A process according to any of the preceding claims, wherein the alkali concentration (as expressed as mole % of  $\text{Na}_2\text{O}$ ) in the said homogeneous admixture is in the range of 0.25 to 7 mole %.

20. A process according to claim 19, wherein the said alkali concentration is within the range from 0.5 to 5 mole %.

21. A process according to any of the preceding claims, wherein the zeolite is crystallised out by heating the said homogeneous admixture under conditions satisfying the following requirements:

$$24 \geq t \exp \left[ 1.3 \times 10^4 \left( \frac{1}{363} - \frac{1}{T} \right) \right] \geq 0.5$$

$$6 - 0.12 t \exp \left[ 1.3 \times 10^4 \left( \frac{1}{363} - \frac{1}{T} \right) \right] \geq \text{CA}$$

wherein  $t$  stands for the crystallising-out time (hr),  $T$  stands for the crystallising-out temperature ( $^\circ\text{K}$ , absolute temperature), and CA stands for an alkali concentration (mole %) in the zeolite-forming homogeneous admixture.

22. A process according to any of the preceding claims, wherein excess alkali metal hydroxide is used and at least a part of the excess alkali metal hydroxide is incorporated in the crystallised-out synthetic zeolite.

23. A process according to claim 22, wherein the synthetic zeolite containing the excess alkali metal hydroxide is neutralised with an inorganic acid, organic acid or acidic salt, which acid or salt has a  $\text{pK}_a$  value of

at least 2, so that the pH of a suspension of the neutralised zeolite is not lower than 9.0.

24. A process according to claim 1 substantially as described in any of the foregoing Examples 1 to 11 with reference to any Sample other than those designated Sample H—.

25. A synthetic type A zeolite detergent builder produced by a process according to any one of the preceding claims.

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COMPLETE SPECIFICATION

2 SHEETS

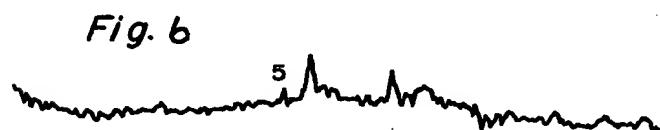
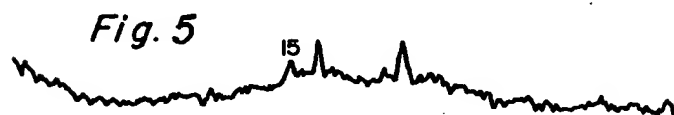
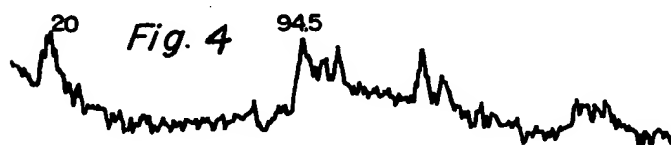
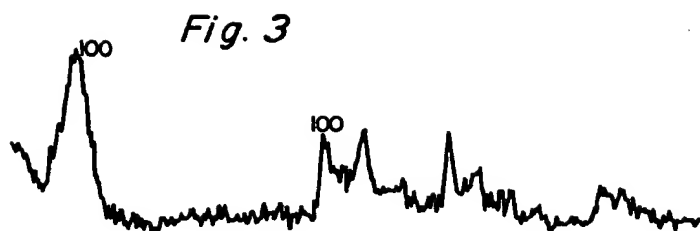
*This drawing is a reproduction of  
the Original on a reduced scale  
Sheet 1*

*Fig. 1*



*Fig. 2*





10 20 30 40  
X-RAY DIFFRACTION ANGLE  $2\theta \rightarrow$